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**NITROGEN-DOPED CARBON AS A CATHODE
MATERIAL FOR LITHIUM-AIR BATTERIES
(POSTPRINT)**

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14. ABSTRACT Lithium-air batteries are among the most promising high energy density electrochemical power sources anticipated to impact future battery technologies. The performance of the cathode in these batteries is a major limiting factor in optimizing the power output of lithium-air batteries. To enhance the performance of the cathode, we investigated incorporating nitrogen in carbon to increase the oxygen reduction reaction activity. Nitrogen doped carbon catalysts were synthesized through chemical treatment of carbon powder with nitrogen. Various techniques like nitrogen adsorption, X-ray powder diffraction, thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray analysis were employed to characterize nitrogen functionality on carbon. The electrochemical behavior of nitrogen doped carbon and commercial carbon for oxygen reduction was examined in 0.1 M KOH using cyclic voltammetry. These studies indicate that the nitrogen functionality on carbon significantly improves the electro-catalytic activity of cathode for oxygen reduction.					
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Nitrogen-Doped Carbon as a Cathode Material for Lithium-air Batteries

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Abstract: *Lithium-air batteries are among the most promising high energy density electrochemical power sources anticipated to impact future battery technologies. The performance of the cathode in these batteries is a major limiting factor in optimizing the power output of lithium-air batteries. To enhance the performance of the cathode, we investigated incorporating nitrogen in carbon to increase the oxygen reduction reaction activity. Nitrogen doped carbon catalysts were synthesized through chemical treatment of carbon powder with nitrogen. Various techniques like nitrogen adsorption, X-ray powder diffraction, thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray analysis were employed to characterize nitrogen functionality on carbon. The electrochemical behavior of nitrogen doped carbon and commercial carbon for oxygen reduction was examined in 0.1 M KOH using cyclic voltammetry. These studies indicate that the nitrogen functionality on carbon significantly improves the electro-catalytic activity of cathode for oxygen reduction.*

Keywords: Nitrogen-doped carbon, X-ray diffraction, scanning electron microscopy, cyclic voltammetry, lithium-air battery.

Introduction

Lithium-air batteries are high energy density electrochemical power sources anticipated to impact future battery technologies.¹ These batteries have significant advantages over conventional electrochemical energy storage and conversion devices.² Abraham and Jiang demonstrated the first nonaqueous, rechargeable lithium-air cell that was based on a solid lithium electrode, a solid polymer electrolyte separator, and a carbon-impregnated solid-polymer electrolyte composite cathode.¹ They achieved capacities of 1600 mAh/g in air, and 1410 mAh/g in a pure oxygen atmosphere. Read *et al* reported even higher cathode capacities of 2120 mAh/g for the Li-air cells. They improved the capacity by designing air cathodes capable of sustaining higher oxygen concentrations.³ Cathode capacities approaching 4000 mAh/g for a Mn based catalyst⁴ and the cathode capacity 5360 mAh/g for the cell employed with a

hydrophobic ionic liquid and lithium salt were reported.⁵ A gravimetric capacity of 5813 mAh/g was achieved using a novel Li-air cathode architecture without the use of catalyst.⁶ Although large gravimetric capacities are obtained, the current density is small. Bruce and co-workers reported a rechargeable Li/O₂ battery using Li₂O₂ and LiCoO₂ electrodes^{7,8}. They report that Li₂O₂ decomposes to yield Li + O₂ on electrochemical charging and that the charge/discharge cycling is sustainable for many cycles.

In our most recent studies, we have fabricated a fully solid state, rechargeable lithium-oxygen battery.⁹ The cell exhibited excellent thermal stability and rechargeability in the 30-105°C temperature range. It was subjected to 40 charge-discharge cycles at current densities ranging from 0.05 to 0.25 mA/cm². Since our approach to fabricate a totally solid-state and rechargeable lithium-air battery is easily scalable, such battery holds a great potential for realization of commercially viable, safe, and lighter lithium-air batteries for applications ranging from electric cars to unmanned aerial vehicles. The performance of the cathode is a major limiting factor in optimizing the power output of lithium-air batteries. To enhance the performance of the cathode, we investigated incorporating nitrogen in carbon to increase the oxygen reduction reaction activity. The doping of these carbon nanostructures with nitrogen atoms is drawing much attention because conjugation between the nitrogen lone-pair electrons and graphene π -systems¹⁰ may create nanomaterials with desired properties. The nitrogen doping of carbon materials has been shown to improve the oxygen reduction reaction activity of carbon¹¹. In this work the role of nitrogen doped carbon with emphasis on the activation process, porosity and surface area measurements is explored. The electrochemical performance of nitrogen doped carbon as cathode for lithium-air battery will be further examined.

Experimental

Morphologies of the carbons were examined using a scanning electron microscope (SEM) on a JEOL microscope equipped with an energy dispersive X-ray (EDX) spectroscopy assembly. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2250 V diffractometer fitted with CuK α as a radiation source at 40 kV and 40 mA. Nitrogen adsorption / desorption

measurements were carried out at 77 K in Micromeritics ASAP 2020. The porosity of cathode materials was carried out on gas pycnometer in Micromeritics, Accu Pyc II 1340. Thermogravimetric analysis (TGA) was carried out on Ketjenblack carbon with and without nitrogen, on a thermogravimetric analyzer (TA Instruments, model 2050). The oxygen reduction activity of these carbon was carried out by cyclic voltammetry in a standard three-electrode cell configuration with 0.1M KOH as the electrolyte using a potentiostat (Solartron, Model1260)) system.

Results and discussion

Figure 1 shows a high magnification SEM micrograph of Ketjenblack carbon. The SEM micrograph reveals the presence of highly dense fibrous and/or spherical carbon. It appears from the SEM micrograph that these fibrous carbons are interconnected with graphitic layers. Energy dispersive X-ray (EDX) analysis was employed to characterize nitrogen functionality on carbon. The EDX conducted on nitrogen doped carbon samples revealed the nitrogen content to be 7.0 at. % (inset of Figure 1). The significant peaks (0 0 2) and (1 0 0) planes were exhibited in the XRD patterns for Ketjenblack carbon and nitrogen doped Ketjenblack carbon. The XRD spectra exhibit a small shift in (1 0 0) reflection for nitrogen doped Ketjenblack carbon. While there was no observable shift in (0 0 2) reflection of nitrogen doped carbon. The reflection (0 0 2) around 23° also indicates the presence of a small domain with parallel stacking of graphene sheets. While the reflection at (1 0 0) around 44° leads to the fibrous/spherical structures formed by sp^2 hybridized carbons and is evident in SEM micrograph. It is also observed from the XRD patterns that the nitrogen doped carbon exhibit the shift in the diffraction peaks.

TGA analysis was employed in air for nitrogen doped Ketjenblack carbon. It is observed that the sample mass does change with temperature below 490°C . Significant mass loss occurs at about 495°C and 521°C for Ketjenblack carbon and nitrogen doped carbon and is due to the carbonization reaction involving breakage of C-C bonds and C-N bonds. The TGA shows that above 650°C there is no further weight loss. TGA shows the higher carbonization temperature for nitrogen doped Ketjenblack carbon in comparison to Ketjenblack carbon. This may be due to incorporation of nitrogen in carbon, as this creates a highly stable and ordered structure of pyridine-like defect sites.

The nitrogen adsorption – desorption isotherms has been conducted and all isotherms show adsorption hysteresis indicating the presence of mesopores. The Brunauer-Emmett-Teller (BET) surface area and pore volume of nitrogen doped carbon were found to be $1532\text{ m}^2/\text{g}$ and $2.4\text{ cm}^3/\text{g}$, respectively. The remarkable nitrogen

uptake above the relative pressure ratio of 0.80 has been observed in BET isotherm and is due to the condensation of nitrogen in a mesoporous carbon. Nitrogen enrichment of carbon helps to tune the pore size in the range 5-20 nm.

In order to investigate the electrocatalytic activity of nitrogen doped Ketjenblack carbon, we ran cyclic voltammetry (Figure 2) on nitrogen doped Ketjenblack carbon and Ketjenblack. We observed the oxygen reduction reaction (ORR) peak at around 0.48 V (SCE) for nitrogen doped Ketjenblack carbon. This peak is absent for Ketjenblack carbon. Further work is required to probe the mechanistic aspects of ORR. Research work is currently underway in this direction.

Conclusion

Incorporation of nitrogen in Ketjenblack carbon improves electrocatalytic ability in ORR. In addition, incorporation of nitrogen in ketjenblack carbon enhances more stable graphite structure with higher surface area and porosity. These initial studies further indicate that nitrogen doped Ketjenblack carbon is a potential cathode material for lithium-air batteries.

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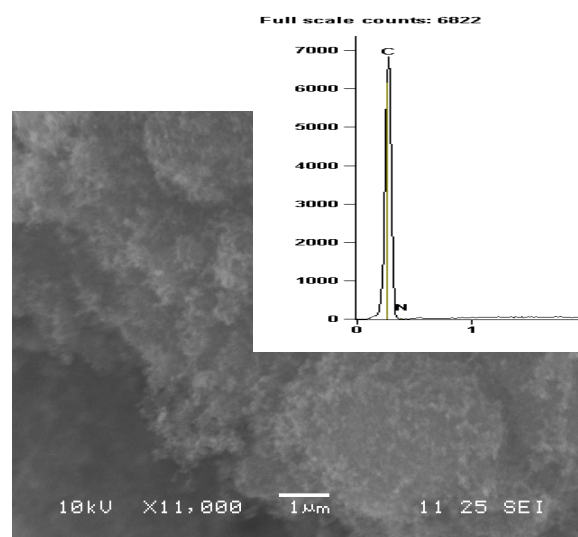


Figure 1: SEM of Ketjenblack carbon with inset of EDX.

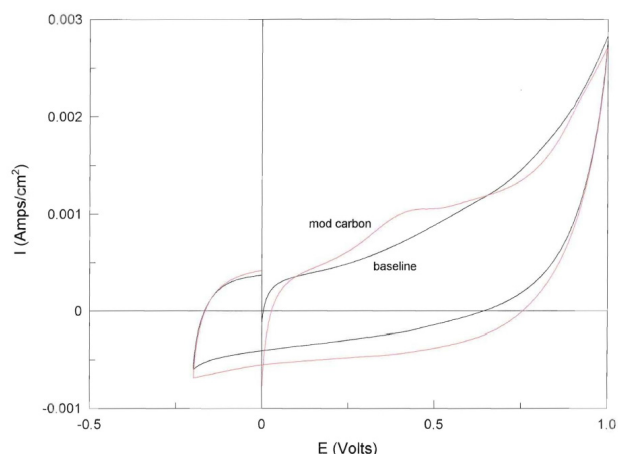


Figure 2: Cyclic voltammograms of Ketjenblack carbon and nitrogen doped Ketjenblack carbon.

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